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Light-Induced Activation of a Molybdenum Oxotransferase Model within a Ru(II)–Mo(VI) Dyad

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ABSTRACT: Nature uses molybdenum-containing enzymes to catalyze oxygen atom transfer (OAT) from water to organic substrates. In these enzymes, the two electrons that are released during the reaction are rapidly removed, one at a time, by spatially separated electron transfer units. Inspired by this design, a Ru(II)–Mo(VI) dyad was synthesized and characterized, with the aim of accelerating the rate-determining step in the cis-dixo molybdenum-catalyzed OAT cycle, the transfer of an oxo ligand to triphenyl phosphine, via a photo-oxidation process. The dyad consists of a photoactive bis(bipyridyl)-phenanthroline ruthenium moiety that is covalently linked to a bioinspired cis-dixo molybdenum thiosemicarbazone complex. The quantum yield and luminescence lifetimes of the dyad [Ru(bpy)2(L2)MoO2(solv)]2+ were determined. The major component of the luminescence decay in MeCN solution (τ = 1149 ± 2 ns, 67%) corresponds closely to the lifetime of excited [Ru(bpy)2(phen-NH2)]3+, while the minor component (τ = 320 ± 1 ns, 31%) matches that of [Ru(bpy)2(H2-L2)]2+. In addition, the (spectro)electrochemical properties of the system were investigated. Catalytic tests showed that the dyad-catalyzed OAT from dimethyl sulfoxide to triphenyl phosphine proceeds significantly faster upon irradiation with visible light than in the dark. Methylviologen acts as a mediator in the photoredox cycle, but it is regenerated and hence only required in stoichiometric amounts with respect to the catalyst rather than sacrificial amounts. It is proposed that oxidative quenching of the photoexcited Ru unit, followed by intramolecular electron transfer, leads to the production of a reactive one-electron oxidized catalyst, which is not accessible by electrochemical methods. A significant, but less pronounced, rate enhancement was observed when an analogous bimolecular system was tested, indicating that intramolecular electron transfer between the photosensitizer and the catalytic center is more efficient than intermolecular electron transfer between the separate components.

INTRODUCTION

Metal-containing oxidoreductases play an important role in biological processes by catalyzing selective oxygenations, in particular, those that involve "green oxygen sources" effectively and under mild conditions, metalloenzymes rely on efficient electron transfer chains that involve spatially separated electron transfer units, such as Fe/S clusters and/or cytochromes to regenerate their active sites (Figure 1, left).1

In the search for functional bioinspired catalysts the importance of an overall design that includes electron transfer components and, in particular, proton-coupled electron transfer is increasingly recognized,4 and a number of second-generation model complexes that contain enzyme active-site mimics that are covalently linked to redox-active units have been reported. Electrochemical approaches, for example, have utilized rapid one-electron transfer components, such as ferrocene.5

These second-generation models represent a significant advancement over conventional molybdenzyme models that catalyze the thermodynamically favorable OAT reaction from sulfoxides to tertiary phosphines, but they do not have additional redox centers built into their design. In these models, the oxidative and reductive half-reaction take place at the Mo center (Figure 1, right). The catalytic activity of these first-generation models is often limited by slow kinetics due to charge build up at the Mo center and the formation of inactive Mo(V) dimers as a result of the overproportionation of Mo(IV) and Mo(V).6

In our search for an advanced design, we were inspired by catalytic systems that exploit photoredox processes, since they offer the opportunity of harnessing solar energy. Because of their high quantum yields, long excitation wavelengths, photostability, and long lifetimes, polypyridine complexes of metal cations with d5 low-spin configuration, such as Ru(II), Re(I), and Ir(III) are frequently used as photoactive units in heterometallic systems to convert light energy to chemical energy. Inspired by photosystem II, manganese model complexes have been linked to [Ru(bpy)3]2+-type photosensitizers to target the four-electron oxidation of H2O by taking advantage of photoinduced electron transfer (PeT).7

Similarly, bioinspired dyads that mimic hydrogenases have been

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studied with the aim of catalyzing the light-driven production of $\text{H}_2$.\textsuperscript{10,11}

Recently, there has been increasing interest in photoredox catalysis\textsuperscript{12--14} and its scope in the photocatalytic oxygenation of organic substrates using clean O atom sources, such as $\text{O}_2$ or $\text{H}_2\text{O}$, which is highly desirable on both environmental and economic grounds. For example, Hamelin and Torelli et al. used a Ru(II)−Cu(II) dyad to oxidize sulfides, phosphines, and alkenes photocatalytically with $\text{O}_2$ as the oxygen atom source and triethanolamine as sacrificial electron donor.\textsuperscript{15} Aukauloo, Banse, and Leibl et al., reported a Ru(II)−Fe(II) dyad that allows the photogeneration of a highly reactive oxo-Fe(IV) center from an Fe(II)-coordinated $\text{H}_2\text{O}$ molecule using $[\text{Co(NH}_3)_3\text{Cl}]^{2+}$ as sacrificial electron acceptor, followed by transfer of the oxygen atom to PPh$_3$.\textsuperscript{16} To drive the photoactivated OAT, the two-electron oxidation of the substrate had to be coupled with two rapid proton-coupled electron transfer steps.

Since Mo is chosen by nature as OAT catalyst par excellence based on its ability to redox cycle between oxidation states $\text{VI}$, $\text{V}$, and $\text{IV}$,\textsuperscript{17} we are interested in utilizing bioinspired Mo complexes as catalysts in dyads designed to facilitate substrate oxidation via a photocatalyst process. Enemark and Kirk et al. already demonstrated in an early study that a Mo center can be photoactivated via an antenna-mediated electron transfer process by covalently linking an oxo-Mo(V) unit to porphyrin-Fe(III) or Zn(II) complexes (Scheme 1a).\textsuperscript{18,19} Although catalytic investigations were not reported for these dyads, the study highlighted photoactivation as a potential way of initiating intercomponent electron transfer. More recently, Heinze et al. appended two redox-active ferrocene units to a cis-dioxo-Mo(VI) complex to mimic the electron-transfer chain in the molybdenum enzyme sulfite oxidase (Scheme 1b).\textsuperscript{7} It was observed that chemical oxidation to the diferrocenium dication greatly accelerated OAT to PMe$_3$, consistent with an accelerated attack of the phosphine at the oxo ligand, coupled with intramolecular electron transfer.

Drawing on these precedents, we anticipated that the addition of a photoactivatable electron acceptor to a cis-dioxo-Mo(VI) center could promote the attack of a phosphine at the oxo ligand in a similar way, thereby increasing catalytic activity. Of the many synthetic ligand systems that were developed in bioinspired approaches to model the function of the molybdenum enzyme,\textsuperscript{20--24} we chose thiosemicarbazones, whose synthesis is straightforward and allows a variety of substituents to be incorporated.\textsuperscript{25--27} We recently reported the electronic fine-tuning of series of six cis-dioxo-Mo(VI) complexes with thiosemicarbazone ligands for OAT and found that electron-withdrawing substituents increase the rate of the OAT to triphenylphosphine, while electron-donating groups have the opposite effect.\textsuperscript{27} This observation is consistent with the generally accepted OAT mechanism, which starts with the nucleophilic attack of the phosphine lone pair on a vacant $\pi^*$ orbital of one of the oxo-ligands, leading to the formation of an oxo-Mo(V) species and phosphine oxide via a phosphine oxide-coordinated intermediate in the rate-determining step.\textsuperscript{28,29} Accordingly, a decrease of the electron density on the cis-dioxo-Mo(VI) center renders the oxo ligand more susceptible to attack and lowers the energy of the transition state by ameliorating negative charge buildup, giving rise to faster reaction rates.

Here, we report the synthesis and the characterization of the Ru(II)−Mo(VI) dyad $[\text{Ru(bpy)}_2(\text{L}^2\text{MoO}_3\text{(solv)})](\text{BF}_4)_2$, in which one coordination site on the Mo(VI) center is occupied by a solvent molecule (Scheme 1c). The photoactive bis(bipyridyl)-phenanthroline ruthenium moiety is linked to the Mo-based OAT catalyst by a methylene group to define the spatial separation while allowing flexibility to facilitate intramolecular electron transfer from the Mo-coordinated thiosemicarbazone ligand to the photo-oxidized Ru$^{III}$bpy−phen$^-$−unit. The photophysical, spectroscopic, and electrochemical properties of the dyad and the results of photocatalytic tests are reported.

### EXPERIMENTAL SECTION

**Materials and Instruments.** Ammonium tetrafluoroborate, paraformaldehyde, 1,10-phenanthroline-5-amine, 4-phenylthiosemicarbazide, and sodium molybdate dihydrate were purchased from Aldrich. Acetylacetic acid was purchased from BDH chemicals, ammonium hexafluorophosphate from Alfa Aesar, salicylaldehyde from Fluka, triethylamine from Fisher Chemicals, and cis-bis(2,2'-bipyridine)-dichlororuthenium hydrate from Acrros organics. $[\text{MoO}_2($acac$)_2]$\textsuperscript{11} and 5-chloromethyl-2-hydroxybenzaldehyde\textsuperscript{32} were synthesized according to reported procedures. Solvents for syntheses were dried and stored...
over 3 Å molecular sieves. \(^{1}\)H and \(^{13}\)C\{\(^{1}\)H\} decoupled NMR spectra were recorded on a Jeol ECOS400 instrument \(^{13}\)C NMR 400 MHz, \(^{13}\)C NMR 100.6 MHz, \(^{15}\)F 376.5 MHz), a Bruker 500 \(^{13}\)C NMR 500 MHz, \(^{13}\)C NMR 125.8 MHz, \(^{31}\)P 202.5 MHz), and a Bruker 700 \(^{13}\)C NMR 700 MHz, \(^{13}\)C NMR 1760 MHz. Assignment of resonances was confirmed based on COSY, DEPT135, and HMQC spectra. Decomposition points were measured with a Stuart Scientific SMP3 apparatus. Elemental analyses of compounds were performed with an Exeter CE-440 elemental analyzer. Electron spray ionization mass spectrometry (ESI-MS) and high-resolution mass spectra were recorded with a Bruker microTOF electrospray mass spectrometer, and mass values are quoted for \(^{19}\)F and \(^{19}\)Mo. UV–visible absorption spectra were measured using an Agilent 8453 spectrometer. Emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Excited-state lifetimes were measured on an Edinburgh Instruments FLS980 fluorescence lifetime instrument.

**Synthesis.** The synthetic method is shown in Scheme 2.

\[ \text{[Ru(bpy)}_2\text{phen-NH}_2\text{]}(\text{BF}_4)_2 \rightarrow \text{cis-Bis(2,2'-bipyridyl)-dichlororuthenium hydrate (1.06 g, 2.04 mmol) and 1,10-phenanthrolinel-5-amine (0.465 g, 2.38 mmol) were dissolved in a mixture of ethanol (160 mL) and water (80 mL). The resulting solution was degassed and refluxed under Ar for 2 h. The ethanol was removed under reduced pressure, and a solution of ammonium tetrafluoroborate (2.14 g, 20.4 mmol) in water was added to precipitate the product as tetrafluoroborate salt. The precipitate was isolated by filtration and washed with water. The crude product was purified by column chromatography on alumina (toluene/acetonitrile 1:1). The product was solubilized in a minimum volume of acetonitrile and reprecipitated with diethyl ether. The bright orange precipitate was isolated and dried under vacuum (1.164 g, 73%).} \]

Decomposition point 283 °C.

\[ ^{1}\text{H NMR (CD}_2\text{CN, 400 MHz):} \delta 8.93 (s, 1H, CHO), 8.72 (d, J = 8.55 Hz, 1H, CH\textsubscript{phen}), 8.54-8.47 (m, 4H, CH\textsubscript{bpy}), 8.16 (d, J = 8.36 Hz, 1H, CH\textsubscript{phen}), 8.11-8.04 (m, 3 CH\textsubscript{bpy} + 1 CH\textsubscript{phen}), 7.99 (s, J = 7.8 Hz, 2H, CH\textsubscript{bpy}), 7.85-7.80 (m, 3H, 2 CH\textsubscript{bpy} + 1 CH\textsubscript{phen}), 7.71 (dd, J = 8.6 Hz, J = 3.64 Hz, 2H, 1 CH\textsubscript{phen} + 1 CH\textsubscript{bpy}), 7.64 (d, J = 5.12 Hz, 1H, CH\textsubscript{phen}), 7.55 (dd, J = 12.4 Hz, J = 5.64 Hz, 2H, CH\textsubscript{bpy}), 7.47-7.40 (m, 3H, 2 CH\textsubscript{bpy} + 1 CH\textsubscript{phen}), 7.24 (m, 2H, CH\textsubscript{bpy}), 6.99 (d, J = 8.6 Hz 1H CH\textsubscript{phen}), 6.90 (s, 1H, CH\textsubscript{phen}), 6.56 (t, 1H, NH), 4.66 (d, J = 4.4 Hz, 2H, CH\textsubscript{bpy}). \]

\[ ^{13}\text{C NMR (CD}_2\text{CN, 125.8 MHz):} \delta 151.6. \]

MS-ESI: m/z 376.5595, \([\text{M}^+\text{]}\) calcd for C\(_{3}\)H\(_{16}\)N-Ru 374.5060. C\(_{17}\)H\(_{16}\)B\(_{3}\)F\(_{3}\)N.Ru + 1.5 H\(_2\)O: Anal. Calcd C 47.49, H 3.49, N 12.12; found C 47.56, H 3.22, N 12.00.

\[ \text{[Ru(bpy)}_2\text{H}_2\text{These results were confirmed by ESI-MS analysis, and the compound was isolated by column chromatography on alumina (toluene/acetonitrile 1:1). The product was solubilized in a minimum volume of acetonitrile and reprecipitated with diethyl ether. The bright orange precipitate was isolated and dried under vacuum (1.164 g, 73%).} \]

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refluxed for 16 h in a solvent mixture of ethanol and acetonitrile (2:1) under nitrogen. After evaporation to dryness the residue was solubilized in a minimum of acetonitrile, and the product was precipitated by addition of ethanol. The product was collected by filtration and dried under vacuum (0.83 g, 74%).

The compound was triturated with diethyl ether and washed with a small volume of argon atmosphere by freeze-drying and dried under vacuum (0.83 g, 74%).

The slope for each compound was obtained from the plot of integrated emission intensity vs absorbance at 470 nm for solutions of [Ru(bpy)3]2+ (black), [Ru(bpy)2(dppe)2]2+ (red), where solv = coordinated solvent molecule, at a range of different concentrations (1–6 μM, deaerated MeCN).

$\Phi$ was determined as the ratio of the integrated emission intensity over absorbance at 470 nm for solutions of [Ru(bpy)3]2+ (black), [Ru(bpy)2(dppe)2]2+ (red), where solv = coordinated solvent molecule, at a range of different concentrations (1–6 μM, deaerated MeCN).

The excited-state lifetime was determined at room temperature (RT) by using [Ru(bpy)3]Cl2 as reference and equation $\tau = \Phi_0 \times \frac{\text{quantum yield of compound } X}{\Phi_0}$, where $\Phi_0$ is the quantum yield of the reference compound ([Ru(bpy)3]Cl2, $\Phi_0 = 0.094 \pm 0.004$) and $\eta$ is the refractive index of the solvent.

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degassed via a minimum of three freeze–pump–thaw cycles using an acetone/liquid nitrogen bath for cooling and research-grade argon for equilibration. Four control samples were prepared in the same way. Sample B had the same composition as sample A but was kept in the dark. Sample C contained [Ru(bpy)3(H2L2)](BF4)2, 300 equiv of PPh3, and 1 equiv of methyl viologen dihexafluorophosphate. Sample D contained [Ru(bpy)3(L2)MoO3(solvo)](BF4)2 (1 mM) and 300 equiv of PPh3, but no methyl viologen dihexafluorophosphate. Sample E contained [Ru(bpy)3]Cl2 (1 mM) plus [MoO2(L2)(solvo)](1 mM), 300 equiv of PPh3, and 1 equiv of methyl viologen dihexafluorophosphate.

Samples A, C, D, and E were irradiated with a Philips 125 W medium-pressure mercury vapor lamp equipped with a water infrared filter and a cutoff filter (λ > 435 nm) for 17 h at a time followed by 7 h of storage in the dark, until almost complete conversion was reached by sample A (9 d). At the beginning and end of each irradiation period, the formation of OPPh3 was monitored by 1H and 31P NMR spectroscopy (H NMR 500 MHz, 31P 202.5 MHz) and by a photograph taken with and without flash to document changes in color and apparent emission intensity.

To account for the different lengths of time taken for the preparation of samples A–E, which required exposure to air and light, the turnover numbers were set to zero at the start of the first irradiation period. This allowed the direct comparison of the samples. In an additional control sample that contained Ph3P (300 mM) in CD3CN/DMSO-d6 (1:1 v/v) under Ar and was left standing at RT for 9 d, only a trace amount of OPPh3 could be detected by 31P NMR.

**Electron Paramagnetic Resonance Spectroscopy.** The electron paramagnetic resonance (EPR) spectra were recorded at X band on a JEOL JES-REX spectrometer. Samples were irradiated in situ with a 100 W mercury vapor arc equipped with a water infrared filter and a cutoff filter (λ > 420 nm). The general EPR parameters were: power 1 mW, field 336.2 mT, scan width ±7.5 mT, modulation width 0.1 mT, time constant 0.1 s, scan time 60 s, modulation frequency 100 kHz, and average of three scans at RT. Sample compositions and concentrations were as follows. Sample 1: [Ru(bpy)3(H2L2)]2+ (0.25 mM) and MV2+ (0.25 mM) in acetonitrile; sample 2: [Ru(bpy)3(L2)MoO3(solvo)]2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile; and sample 3: [Ru(bpy)3(L2)2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile/DMSO (1:1 v/v). All measurements were performed in glass capillaries at RT and under Ar.

### RESULTS AND DISCUSSION

**Synthesis and Characterization of [Ru(bpy)3(L2)2+ (0.25 mM) and MV2+ (0.25 mM) in acetonitrile; sample 2: [Ru(bpy)3(L2)MoO3(solvo)]2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile; and sample 3: [Ru(bpy)3(L2)2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile/DMSO (1:1 v/v). All measurements were performed in glass capillaries at RT and under Ar.**

**Electronic Absorption and Emission Spectra.** The electronic absorption spectrum of [Ru(bpy)3(L2)2+ (0.25 mM) and MV2+ (0.25 mM) in acetonitrile; sample 2: [Ru(bpy)3(L2)MoO3(solvo)]2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile; and sample 3: [Ru(bpy)3(L2)2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile/DMSO (1:1 v/v). All measurements were performed in glass capillaries at RT and under Ar.**

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The lifetime of the Ru-based component of the dyad, with \( \lambda_{em} = 449 \text{ nm, } \epsilon_{em} = 15 700 \text{ M}^{-1} \text{cm}^{-1} \), \( \lambda_{max} = 618 \text{ nm, MeCN} \)).

If solutions with equal absorbance at 470 nm are compared, the emission intensity of the molybdenum-containing dyad [Ru(bpy)3(L2)2+ (0.25 mM) and MV2+ (0.25 mM) in acetonitrile; sample 2: [Ru(bpy)3(L2)MoO3(solvo)]2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile; and sample 3: [Ru(bpy)3(L2)2+ (0.25 mM), PPh3 (75 mM) and MV2+ (0.25 mM) in acetonitrile/DMSO (1:1 v/v). All measurements were performed in glass capillaries at RT and under Ar.**

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Figure 3. Emission decay profiles obtained at 620 nm (λ_em = 470 nm) under Ar for 1 × 10^{-5} M solutions of [Ru(bpy)_2(phen-NH_2)]^{2+} (blue), [Ru(bpy)_(H_2-L^2)]^{2+} (green), [Ru(bpy)_2(L^2)MoO_4(solv)]^{2+} (red), and [Ru(bpy)_2(L^2)MoO_4(solv)]^{2+} with 100-fold excess of Ph_3P (black) in MeCN.

Figure 4. CV of [Ru(bpy)_2(L^2)MoO_4(solv)](BF_4)_2 (scan range: from 0 to +1.7 V and from −2.0 to 0 V (red); between 0 and +1.7 V (green) and between 0 and −2 V (blue); 1 mM with 0.1 M [Bu_4N][BF_4]) in anhydrous DMF, potentials vs Ag/AgCl, scan rate 100 mV s^{-1}.

Table 1. Quantum Yields (Φ) of Luminescence and Lifetimes (τ) of the MLCT States in MeCN

<table>
<thead>
<tr>
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<th>Φ_{ex}^{a,b}</th>
<th>τ (ns)(^{\text{c}})</th>
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<tr>
<td>[Ru(bpy)_2(phen-NH_2)]^{2+}</td>
<td>0.078 ± 0.003</td>
<td>1100 ± 1</td>
</tr>
<tr>
<td>[Ru(bpy)_2(H_2-L^2)]^{2+}</td>
<td>0.076 ± 0.003</td>
<td>303 ± 1 (40%), 1100 ± 2 (60%)</td>
</tr>
<tr>
<td>[Ru(bpy)_2(L^2)MoO_4(solv)]^{2+}</td>
<td>0.044 ± 0.002</td>
<td>119 ± 0.1 (2%), 320 ± 1 (31%), 1149 ± 2 (67%)</td>
</tr>
<tr>
<td>[Ru(bpy)_2(L^2)MoO_4(solv)]^{2+} + Ph_3P</td>
<td>not determined</td>
<td>8.1 ± 0.1 (1%), 290 ± 1 (31%), 1037 ± 1 (68%)</td>
</tr>
</tbody>
</table>

\(^{a}\text{Argon atmosphere, 1 × 10^{-5}}\text{ M in MeCN, [Ru(bpy)_2]Cl_2 reference: }\Phi = 0.094 ± 0.004, \lambda_{em} = 470 \text{ nm, } \lambda_{exc} = 620 \text{ nm, error margins represent one standard deviation and are propagated from the standard error in the fitted gradients (plot shown in Figure 2b)).}\(^{b}\text{λ}_{em} = 470 \text{ nm, } \lambda_{exc} = 620 \text{ nm. Error margins represent one standard deviation.}\)

of the longest-lived component of 1149 ± 2 ns resembles those obtained for [Ru(bpy)_2(phen-NH_2)]^{2+} and [Ru(bpy)_2(H_2-L^2)]^{2+}, and the close to statistical contribution of 67% suggests that it is due to decay from a bpy-localized excited state. The second lifetime of 320 ± 1 ns resembles that of the shorter-lived component obtained for [Ru(bpy)_2(H_2-L^2)]^{2+}, and again, the close to statistical contribution of 31% indicates decay from a H_2-L^2-centered excited state. An additional minor (2%) shorter-lived component with τ = 11.9 ± 0.1 ns has to be added to fit the data satisfactorily.

The spectroscopic investigations show that the covalently linked catalytic unit of the dyad decreases the quantum yield of the photoactive unit. On the one hand, in similar systems, quenching via intramolecular photoinduced electron transfer from an appended electron-rich phenolate ligand to a photoexcited metal-based luminophore, such as RuIII(bpy)_3, has been observed using time-resolved absorption spectroscopy. On the other hand, the addition of a 100-fold excess of Ph_3P does not have a significant effect on the three lifetimes obtained for [Ru(bpy)_2(L^2)MoO_4(solv)]^{2+} (Figure 3 and Table 1), confirming the absence of an intramolecular quenching effect of the substrate.

**Electrochemistry.** The cyclic voltammogram (CV) of [Ru(bpy)_2(L^2)MoO_4(solv)](BF_4)_2, recorded between −2 and 1.7 V in dry DMF using [Bu_4N][BF_4] as the supporting electrolyte, shows several redox processes that are also evident in the CVs of its components (Figure 4, Figures S1–S3, and Table 2). In the positive region, an irreversible oxidation wave is observed that involves the transfer of approximately two electrons, based on the comparison with the peak currents associated with the reversible processes in the negative potential region. One of the overlapping oxidation steps can be assigned to the oxidation of Ru(II) to Ru(III) by comparison with electrochemical data obtained for [Ru(bpy)_3]Cl_2 under analogous conditions (Table 2 and Figure S1), previously reported oxidation potentials for similar Ru(II) complexes, and spectro-electrochemical investigations (see below). The overlapping second irreversible oxidation process is associated with the molybdenum-coordinated thiosemicarbazone. A comparison with the CVs obtained for [MoO_2(L^3Me)-Cl_2] and H_2-L^3Me under analogous conditions (Figures S2 and S3), and observations reported for similar Mo(VI)-semicarbazone complexes, provide further evidence for this assertion. It is known that a one-electron oxidation of thiosemicarbazones can lead to dimerization via disulfide-bond formation, while a two-electron oxidation can lead to cyclization and formation of 1,2,4-triazole-3-thione or 1,3,4-thiadiazole rings. The latter is in accordance with the irreversibility and high peak current of the oxidation process observed at a peak potential (E_{pox}) of 1.43 V in the CV of [MoO_2(L^3Me)(solv)] (Table 2).

In addition, there are weak irreversible waves at E_{pox} = 0.58 and 1.07 V and E_{pred} = −0.27, −0.72, and −1.12 V that can be assigned to the Mo-containing unit and/or its degradation products as similar waves are observed in the CV of [MoO_2(L^Me)(solv)] (Figure S2). While the shoulder at −1.12 V lies within the potential range typically associated with the reduction of Mo(VI) to Mo(V)\(^{40,41}\) the irreversible reduction waves at −0.27 and −0.72 V are only present if the positive potential range is scanned first (Figure 4). Hence, these two reduction processes appear to be associated with chemical reaction products formed upon oxidation.

By comparison with the CV of [Ru(bpy)_3]Cl_2 (Table 2 and Figure S1) and literature data, the three irreversible waves at E_{1/2} = −1.22, −1.41, and −1.75 V can be assigned to three successive one-electron reductions of the Ru-polypyrpyridine unit.
Figure 5. Difference spectra obtained during the spectro-electrochemical oxidation of \([\text{MoO}_2(\text{L}^{\text{Me}})\text{MeOH}]\) (0.5 mM) recorded at \(E_{\text{app}} = 1.5\ V\) after 1, 2, 3, 4, 6, 8, 10, 12, 15, 18, 21, 25, 30, 35, and 40 min (carbon veil electrode).

Spectro-Electrochemical Oxidation. \([\text{Ru(bpy)}_2(\text{L}^{\text{2}})\text{MoO}_2(\text{sol})][(\text{BF}_4)_2]\) was oxidized electrochemically at 1.5 V using a carbon veil electrode, and the difference spectra were recorded (Figure 5). Two negative bands (bleaches) developed over time at 360 and 470 nm, while the absorbance below 340 nm increased, and a weak and broad band developed over time at 360 and 470 nm, while the spectral changes observed below 400 nm are likely, an intramolecular cyclization of the ligand, as reported for structurally related thiosemicarbazones.

For comparison, the reference compound \([\text{MoO}_2(\text{L}^{\text{Me}})\text{MeOH}]\) was oxidized electrochemically at 1.5 V after 5 s and after 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18, 20, 23, 26, 30, and 35 min (carbon veil electrode). The spectroscopic profiles obtained upon electrochemical reduction (−1.2 V) are shown in Figure 7. Two positive bands rise at 390 and 510 nm as well as two negative bands at 350 and 450 nm.

Similarly, \([\text{Ru(bpy)}_3]\text{Cl}_2\) and \([\text{MoO}_2(\text{L}^{\text{Me}})\text{MeOH}]\) were reduced at the same potential (Figures S5 and S6). A comparison of the spectra obtained for the complexes shows that the dyad behaves similarly to \([\text{Ru(bpy)}_3]\text{Cl}_2\) above 400 nm, while the spectral changes observed below 400 nm are consistent with the reduction of both the ruthenium and the molybdenum moieties.

A reduction of the dyad was then performed at −1 V (Figure 8a) to investigate if it is possible to selectively reduce only the Mo-based catalytic center. The profile obtained is very different from that observed in the case of \([\text{MoO}_2(\text{L}^{\text{Me}})\text{MeOH}]\), which is consistent with the reduction of both moieties in the dyad.
from that recorded for the dyad upon reduction at the more negative potential of −1.2 V (Figure 7). A positive band at 490 nm and three overlapping negative bands in the region between 300 and 450 nm grow in over time. The positive band resembles the corresponding band in the spectrum of the molybdenum complex (Figure 8b). Despite the absence of the small positive band at 360 nm, the absorbance between 300 and 450 nm decreases, whereas it increases when [Ru(bpy)$_3$]Cl$_2$ is reduced.

The spectrum obtained upon electrochemical reduction of [Ru(bpy)$_3$]$_2$(L$^3$)MoO$_2$(solv)](BF$_4$)$_2$ at −1 V was then compared with the spectrum obtained after the stoichiometric chemical reduction of the dyad, which was performed at a 25 μM concentration in MeCN in the absence of an O atom donor. To ensure complete reduction of the Mo-based unit (turnover number = 0.5) a 100-fold excess of the O atom acceptor PPh$_3$ was used. The initial spectrum of [Ru(bpy)$_3$]$_2$(L$^3$)MoO$_2$(solv)](BF$_4$)$_2$ was subtracted from the spectrum recorded after chemical reduction, to obtain a difference spectrum (Figure 8b). The profiles of the spectra obtained after electrochemical and chemical reduction are very similar. Therefore, the spectro-electrochemical measurements confirm that the molybdenumbased moiety can be selectively reduced at −1 V, while the reduction of the ruthenium-based moiety requires a more negative potential.

**Photoactivated Oxygen Atom Transfer Catalysis.** The catalytic activity of the dyad was investigated using triphenyl phosphine as the oxygen acceptor and DMSO as the oxygen donor. Under an atmosphere of argon, a solution containing [Ru(bpy)$_3$]$_2$(L$^3$)MoO$_2$(solv)]$^{2+}$ (1 mM), triphenyl phosphine (300 equiv), and methyl viologen (MV$^{2+}$, 1 equiv) in a mixture of deuterated acetonitrile/DMSO (1:1) was subjected to alternating cycles of irradiation with >435 nm light (17 h) followed by dark storage (7 h). At the beginning and end of each irradiation period, the formation of triphenyl phosphine oxide was monitored by $^1$H and $^{31}$P NMR spectroscopy. As evident from Figure 9, the reaction proceeded significantly faster during the periods of light exposure than in the dark. After a total irradiation time of 154 h, 95% completion was reached, and the presence of dimethyl sulfide in the sample was clearly detectable by its characteristic smell. The catalyst proved to be remarkably stable under these conditions, with the turnover number only limited by the solubility of triphenyl phosphine in DMSO/acetonitrile (1:1) without further losses. The $^1$H NMR spectra of sample A were examined before and after each irradiation period to monitor the integrity of the catalyst. Even after a total irradiation time of 154 h, the proton resonances of the dyad remained essentially unchanged (Figure S8).

A control experiment in which an analogous solution was kept in the dark all the time (sample B, Figure 9) produced much less of the oxidation product, indicating that the thermal conversion rate is much slower than the photochemical conversion. Again, the $^1$H NMR spectra recorded during the thermal reaction showed evidence for either catalyst decomposition or the formation of LMo(O)-O-Mo(O)L dimers (Figure S9). A control sample containing [Ru(bpy)$_3$]$_2$(H$_2$L$^3$)MoO$_2$(solv)]$^{2+}$ (1 mM) and 300 equiv of triphenylphosphine but no methyl viologen (sample D) yielded a similar amount of product to the dark control after irradiation for a total of 154 h (Figure 9), demonstrating that methyl viologen accelerates the reaction in the presence of light. A control sample containing [Ru(bpy)$_3$]$_2$(H$_2$L$^3$)MoO$_2$(solv)]$^{2+}$ but no molybdenum (sample C) was found to produce less...
Bleaching of the even 1 h after stopping the irradiation, since the catalytic Mo center was missing. In this sample, a subsequent OAT could not take place, with and without flash (sample A: [Ru(bpy)]₂,(L²)(MoO₃(sol))²⁺, 300 equiv of PPh₃ and 1 equiv of MV²⁺; sample B: control kept in the dark; sample C: [Ru(bpy)][(H₂-L²)]²⁺, 300 equiv of PPh₃ and 1 equiv of MV²⁺; sample D: [Ru(bpy)][(L²)MoO₃(sol)]²⁺, 300 equiv of PPh₃ but no MV²⁺; sample E: [Ru(bpy)]²⁺ plus [MoO₃(LMe₃)(sol)], 300 equiv of PPh₃ and 1 equiv of MV²⁺).

These observations are consistent with a mixture that contains the orange and luminescent Ru(II)-based photosensitizer unit and dark blue-green MV⁺⁺, one of the products of the oxidative quenching of the RuIII-bpy/phen⁺⁺ MLCT excited state by MV²⁺, which initially produces RuIII-bpy/phen and MV⁺⁺. While in the absence of other reductants, back electron transfer from MV⁺⁺ to RuIII occurs on the nanosecond time scale, in our case the MV⁺⁺ radical is much longer-lived (see below). In accordance with the irreversible oxidative wave seen in the CV of the dyad and its emission lifetimes, we propose that fast reduction of the RuIII center occurs via electron transfer from MV⁺⁺ to RuIII, which would be expected upon oxidation of RuII to RuIII. To confirm this proposal, the absorption spectra of sample A were recorded before irradiation, immediately after selected irradiation intervals, and after storage in the dark. The characteristic absorption bands due to MV⁺⁺ at λmax 397 and 609 nm emerge during irradiation (Figure 11). Bleaching of the ³MLCT band (λ₂₄ₑ = 455 nm), which would be expected upon oxidation of RuII to RuIII, is not observed. Consequently, the rereduction of the photooxidized RuIII to RuII has occurred on the time scale that it took to record the absorption spectrum (~2 min). However, the MV⁺⁺ radical is still present and hence is not the source of the reducing equivalent.

During the storage periods in the dark, the color of both NMR samples (A and E) returned to orange, and the emission was restored, indicating that the resting state of the Ru(II)-based photosensitizer is regenerated and the MV⁺⁺ radical cation is reoxidized to MV²⁺ (Figure 10b). Light is not required for this reaction to proceed. The electronic absorption spectra confirm a decrease in the MV⁺⁺ concentration in the dark, with the spectrum resembling that obtained after 1 h of irradiation (Figure 11).

**Electron Paramagnetic Resonance Spectroscopy.** In addition, EPR spectroscopy was used to monitor radical formation. During in situ irradiation of a solution containing [Ru(bpy)]₂,(H₂-L²)]²⁺ (0.25 mM) and MV²⁺ (0.25 mM) in acetonitrile, a strong EPR signal due to MV⁺⁺ was observed (Figure 12, Sample 1). Even 1 h after stopping the irradiation,
66% of the original MV** signal remained, confirming that the radical is long-lived and back electron transfer from MV** to the complex, most likely an oxidized form of the ligand H₂L², is very slow. However, a H₂L²-based radical could not be detected, since the spectrum was dominated by the intense MV** signal.

During in situ irradiation of a sample containing [Ru(bpy)₂(H₂L²)MoO₃(solv)]²⁺ (0.25 mM), PPh₃ (75 mM), and MV²⁺ (0.25 mM) in acetonitrile (no DMSO), a clear signal due to MV** was observed (Figure 12, Sample 2). In line with the lower quantum yield of the dyad, the signal was weaker than that observed with [Ru(bpy)₂(H₂L²)]²⁺. An L²-based radical or paramagnetic Mo species could not be detected. Again, the strong signal of the exceptionally stable MV** radical is likely to mask any signals of shorter-lived radical species.

Subsequently, DMSO was added to the dyad-containing sample, and the EPR spectrum was recorded, while the sample was irradiated. In this case, a weaker signal due to MV** was observed (Figure 12, Sample 3). The decrease is consistent with the expected decrease of the MV** concentration under turnover conditions. In the dark, the signal decayed, with ~33% of the original intensity remaining after 1 h. Again, ligand- or Mo-based signals could not be detected, since the spectrum was dominated by the MV** signal.

**Proposed Catalytic Cycle.** On the basis of our observations and the information obtained from photophysical, spectroscopic, and electrochemical investigations, the following catalytic mechanism is proposed (Scheme 3). In the first step of the photoredox cycle, the photoexcited dyad [RuII⁺(bpy)₂(L²)-MoO₃(solv)]²⁺ is oxidatively quenched by MV²⁺ to give [RuIII⁺(bpy)₂(L²)MoO₃(solv)]²⁺ and MV**, as evidenced by the change in color from orange to dark blue-green, the EPR spectra, and the loss of emission. The oxidized dyad then undergoes fast intramolecular electron transfer to form [RuII⁺(bpy)₂(L²)MoO₃(solv)]²⁺, where L² represents the oxidized form of Mo-coordinating phenol–thiosemicarbazone ligand. This proposed step of the photoredox cycle is supported by both the visible spectra obtained shortly after irradiation and the irreversible oxidative wave in the cyclic voltammogram of the dyad. As a consequence, back electron transfer from MV** to RuIII is outcompeted. The presence of MV** is clearly seen in Sample C, where the deep blue-green color of MV** persists, since the catalytic OAT cycle cannot turn over in the absence of molybdenum.

In the presence of molybdenum (sample A), the subsequent OAT to PPh₃ gives OPPh₃, which was detected by NMR spectroscopy, and a species with an electronic absorption spectrum that closely resembles that obtained for the species generated by electrochemical reduction, tentatively assigned as [RuII⁺(bpy)₂(L²)MoO₃(solv)]²⁺. The reductive half-reaction with DMSO produces DMS and regenerates MV²⁺ and RuII⁺(L)MoO₃(O)solv. While in-depth investigations are required to determine the exact mechanistic and kinetics details, in particular, of the reductive half-reaction, our tests show that the photoactivated OAT cycle runs significantly faster than the thermal OAT cycle, which proceeds in the absence of light.
The Ru(II)–Mo(VI) dyad \([\text{Ru(bpy)}_3^2(\text{L}^2\text{MoO}_2\text{solv})]^2^+\) was synthesized, fully characterized, and shown to accelerate the rate-determining step in the cis-dioxo molybdenum-catalyzed OAT cycle, the transfer of an oxo ligand to PPh\(_3\) via a photoredox process. The energy provided by visible light is sufficient to generate a highly reactive, oxidized form of the molybdenum-centered catalyst, in which the noninnocent phenol–thiosemicarbazone ligand plays key role. The single electron transfer (SET) step in the photoredox process is essential in making the reactive one-electron oxidized form of the thiosemicarbazone complex accessible. In contrast, electrochemical methods trigger an irreversible two-electron oxidation process. Methylviologen acts as a mediator in the photoredox cycle, the rate acceleration of the OAT can be switched on and off via the light source.

The dyad can be regarded as an advanced bioinspired model for Mo-containing oxotransferases, since it demonstrates the importance of both spatially separated one-electron transfer units and the participation of a noninnocent S-containing ligand in OAT catalysis.

Interestingly, significant rate enhancement was also observed when two separate sensitizer and catalyst components were tested. Even though the effect seen with the bimolecular system was less pronounced than that observed with the covalently linked dyad, the reduced synthetic effort allows for the testing of different catalyst-sensitizer combinations and a higher-throughput approach could facilitate the discovery and optimization of new photoredox-catalytic systems in the future.

**ASSOCIATED CONTENT**

- Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01483.

  CVs of \([\text{Ru(bpy)}_3]^2\text{Cl}_2\), \([\text{MoO}_2(\text{L}^\text{Me})\text{(solv)}]_2\text{H}^2\text{L}^\text{Me}\), and methyl viologen dichloride; spectro-electrochemical information provided by control compounds; photograph of samples A–E before irradiation; EPR simulation parameters, \(\text{H}^1\) and \(\text{P}^3\) NMR spectra recorded after irradiation for samples A, C, D, and E; NMR spectra and mass spectra of synthesized compounds. (PDF)

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